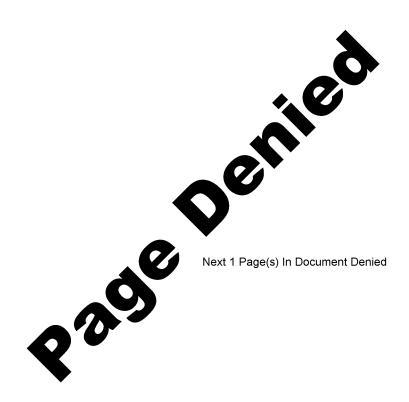
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OXIDATION OF PHENOL IN A FIELD OF ULTRASONIC WAVES

Yu. Yu. Lur'ye, P. F. Kandzas, and A. A. Mokina

The methods used for purifying any types of sewer waters of industrial enterprises are frequently unprofitable. This gives rise to the necessity of seeking new methods of purification.

It is expedient to test the use of ultrasonic vibrations in the field of the purification of industrial sewer waters.

The influence of ultrasonic vibrations on aqueous solutions of phenol has been studied [1]; however, no complete analysis of its decomposition products has been performed.

In our investigations we used an ultrasonic setup consisting of a high frequency tube generator with a power of 1500 watts and an ultrasonic vessel with a piezoquartz emitter. The vibrational frequency was 800 kilocycles per second. Aqueous solutions of phenol with concentrations of 25-300 mg/liter were subjected to the action of ultrasonic vibrations under various physical conditions of the experiment. To maintain the necessary pH, we added buffer solutions, the stability of which to the action of vibrations was preliminarily checked.

It is known that the action of ultrasonic vibrations on water containing dissolved air leads to the formation in it of nitrous and nitric acids [2, 3]. Although the concentration of these acids is relatively low even after prolonged influence of the vibrations, however, nitration products may form, since, according to the data of [4], when water saturated with benzene is "sonicated", nitrobenzene is formed in it. The process of nitration of phenol should be promoted by the nitrous acid formed, the catalytic action of which has been demonstrated [5]. It is known [1] that incorporation of the OH-group into the benzene ring is observed during sonication, resulting in the formation of phenol. Hence it was natural to expect that the action of ultrasonic vibrations on an aqueous solution of phenol might lead to the formation of polyatomic phenols.

The first investigations showed that the oxidation of phenol occurs during sonication, leading to the formation of pyrocatechol, pyrogallol, and traces of hydroquinone. Resorcinol was not detected. It was also established that small amounts of mononitrophenols are formed in strongly

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acid medium.

Preliminary experiments on the quantitative determination of the oxidation products of phenol showed that the material balance is far from 100%. We were able to determine only 85.22 mg/liter in an average for two experiments, converted to phenol, with its initial concentration in solution of 96 mg/liter, which came to 88.75%.

We assumed the possibility of the formation of subsequent oxidation products as well -- quinones and unsaturated acids, the partial purging of phenol from solution [6], and the formation of formaldehyde, which was detected in [1]. Experiments on the action of ultrasonic vibrations both on aqueous solutions of phenol and on its primary oxidation products showed the following.

After only 15-20 min of sonication at an intensity of 4 watts/cm2 (volume 400 ml) of a solution of hydroquinone in 25 mg/liter concentration, the golden-yellow color characteristic of a freshly prepared solution of p-quinone was observed. The qualitative reaction [7] showed its presence. The concentration of p-quinone in solution after an hour of the action of ultrasonic vibrations was 4.7 mg/liter. Sonication of a solution of pyrocatechol of the same concentration under these conditions also led to its rather rapid oxidation. Its residual content was 11 mg/liter, which corresponds to 56% oxidation. Moreover, we determined 6.05 mg/liter of o-quinone. In the investigation of a phenol solution with concentration 48 mg/liter (volume 400 ml), sonicated for 1 hour at an intensity of 4 watts/cm2, we found a small amount of o-quinone, traces of p-quinone, and formaldehyde. After prolonged exposure of a concentrated pyrocatechol solution in an ultrasonic field, we succeeded in obtaining crystals of muconic acid. To establish the purgibility of phenol, we conducted an experiment in a closed vessel, the outlet from the upper part of which was submerged in an absorbing solution. O.1N NaOH was used as the latter. The investigations showed that under the influence of ultrasonic vibrations negligible purging of phenol occurs; its concentration in the absorbing solution was 0.34 mg/liter after 45 min. A solution of phenol with a concentration of 96 mg/liter was sonicated at an intensity of 4 watts/cm2; the solution volume was 350 ml. The results of a quantitative determination of the oxidation products of phenol are presented in Table 1, from which we can see that the total amount of substances, converted to phenol, without considering the oxidation products of pyrogallol and the quinones, was 91.78 mg/liter, or 95.5% of the initial phenol.

The curves of Fig. 1 illustrate the kinetics of the process of phenol oxidation, in which the primary oxidation products -- polyatomic phenols -- undergo further transformations.

While the phenol concentration decreases continuously with increasing duration of the sonication, the amount of polyatomic phenols increases only during the first period, and drops after reaching a maximum. At the same time, a gradual increase is observed in the o-quinone concentration. Under the more prolonged action of ultrasonic vibrations, the curve of the variation of the o-quinone concentration probably takes a form analogous to the curves of polyatomic phenols.

Table 1*

* Average data from two experiments are cited. Sonication was performed in a closed vessel.

Key to Table 1:

- 1. Volume of sonicated solution, ml
- 2. Intensity of sounds, watts/cm2
- 3. Duration of sonication, min
- 4. Initial phenol concentration, mg/liter
- 5. Determined after sonication, mg/liter
- 6. Converted to phenol, mg/liter
- 7. Phenol
- 8. Pyrocatechol
- 9. Pyrogallol
- 10. o-quinone
- 11. p-quinone
- 12. Formaldehyde
- 13. Pyrocarechol
- 14. Pyrogallol
- 15. o-quinone
- 16. Total calculated on the basis of phenol, mg/liter
- 17. Percent of initial phenol
- 18. Traces

In order to determine the optimum conditions of the oxidation of phenol, we studied the influence of the medium, initial phenol concentration, intensity of the vibrations, and duration of sonication on the process. The decomposition of phenol is independent of the reaction medium within a broad range of pH values. When the pH varies in the range 3-9, practically the same oxidation effect is obtained. Only in a strongly alkaline medium is any significant deceleration of the process observed. An analogous picture was observed in experiments on the oxidation of phenol by the oxygen of the air [8].

Fig. 1. Variation of the concentration of phenol and the basic products of its oxidation during the process of sonication: 1 -- phenol; 2 -- pyrocatechol; 3 -- pyrogallol; 4 -- oquinone; volume 400 ml, intensity of ultrasound 6 watts/cm2. Key: 1) c, mg/liter; 2) t, hrs.

Fig. 2. Dependence of the process of oxidation on the concentration of phenol in solution. Volume of solution 400 ml, intensity of ultrasound 4 watts/cm², duration of sonication

Key: 1) amount of oxidized phenol, mg/liter; 2) c,mg/liter.

We can see from Fig. 2 that under the same physical conditions of the experiment, the amount of oxidized phenol increases with increasing phenol concentration up to a definite limit (~300-500 mg/liter). A further increase in it exerts no effect on the rate of the process. The curves of Fig. 3 show that as the vibrational intensity is increased, the on that ten increment. Atthough in a phone period of action of vibrations on a phenot adultion with a concentration of his mg/liter at an intensity of watta/cm², 98.1% was existed, at an intensity of h watta/cm² during this same period only 73.6% of the phenol was existed. As the phenol content in the solution is reduced, the rate of the decomposition process drops. Small amounts of phenol, remaining in solution after prolonged influence of vibrations, are existed with considerably greater difficulty.

Fig. 3. Dependence of the process of oxidation of phenol on the duration of sonication at various intensities: 1 -- 4 watts/cm²; 2 -- 6 watts/cm²; 3 -- 7 watts/cm²; phenol concentration in solution 48 mg/liter, solution volume 400 ml.
Key: 1) oxidized phenol, %; 2) t, hrs.

To obtain a general idea of the influence of ultrasonic vibrations on the simplest aromatic hydrocarbons, we supplemented our investigation with a small number of experiments in which an aqueous solution of benzene was subjected to the action of ultrasound. As we can see from the data presented in Table 2, in addition to formaldehyde, we also determined phenol, pyrogallol, and pyrocatechol in considerable amounts.* During the process of sonication of a benzene solution, we observed its gradual clouding, and the appearance of the specific odor of phenol alcohols. This enabled us to assume that phenol condensed with formaldehyde.

An acidified solution of benzene (volume 300 ml) with a concentration of 500 mg/liter was subjected to the action of ultrasound at an intensity of the order of 4-5 watts/cm². During the process of sonication, which lasted for ~ 5 hours, benzene was supplementarily introduced into the reaction vessel twice in small doses. The temperature was kept in the range $\sim 40-42^{\circ}$. The experiment confirmed our hypotheses. After the sonicated solution was allowed to stand at 60° , a resin precipitated.

The results of the investigations conducted and an acquaintance with the literature data enabled us to outline the following scheme of the process of decomposition of the benzene ring under the action of

^{*} Formaldehyde and phenol hydroxyls were also found in the experiments of [1].

Table 2

Key to Table 2:

- 1. Volume of sonicated solution, ml
- 2. Intensity of sound, watts/cm2
- 3. Duration of sonication, hrs
- 4. Benzene concentration in solution, mg/liter
- 5. Determined after sonication, mg/liter
- 6. Formaldehyde
- 7. Phenol
- 8. Pyrocatechol
- 9. Pyrogallol
- 10. Hydroquinone
- 11. Traces

ultrasonic vibrations (Fig. 4).

Fig. 4. Key: 1) decomposition products.

The oxidation of phenol, in our opinion, is caused mainly by the action of free radicals, formed as a result of the decomposition of water molecules under the action of ultrasonic vibrations.

CONCLUSIONS

- 1. The sonication of aqueous solutions of benzene and phenol leads to the decomposition of the benzene ring. On the one hand, there is a successive oxidation of the ring, leading to the formation of phenol, polyatomic phenols (pyrocatechol, pyrogallol, hydroquinone), quinones, and ultimately unsaturated acids. On the other hand, a direct decomposition of the benzene molecule occurs, forming formaldehyde. The latter, condensing with phenol under definite conditions, forms phenol-formaldehyde resins.
- 2. Prolonged sonication of aqueous solutions of phenol in strongly acid medium leads to the formation of small amounts of mononitrophenols.
- 3. The decomposition of phenol proceeds to the same degree in acid, neutral, and weakly alkaline media. A strongly alkaline medium produces a considerable deceleration of the process.
- 4. The decomposition of phenol depends on its initial concentration in solution. Under the same physical conditions of the experiment, the amount of oxidized phenol increases with increasing concentration to a definite limit, above which an increase in it has no effect on the rate of the process.
- 5. The decomposition of phenol depends on the vibrational intensity. As the latter is increased, the rate of the process increases.

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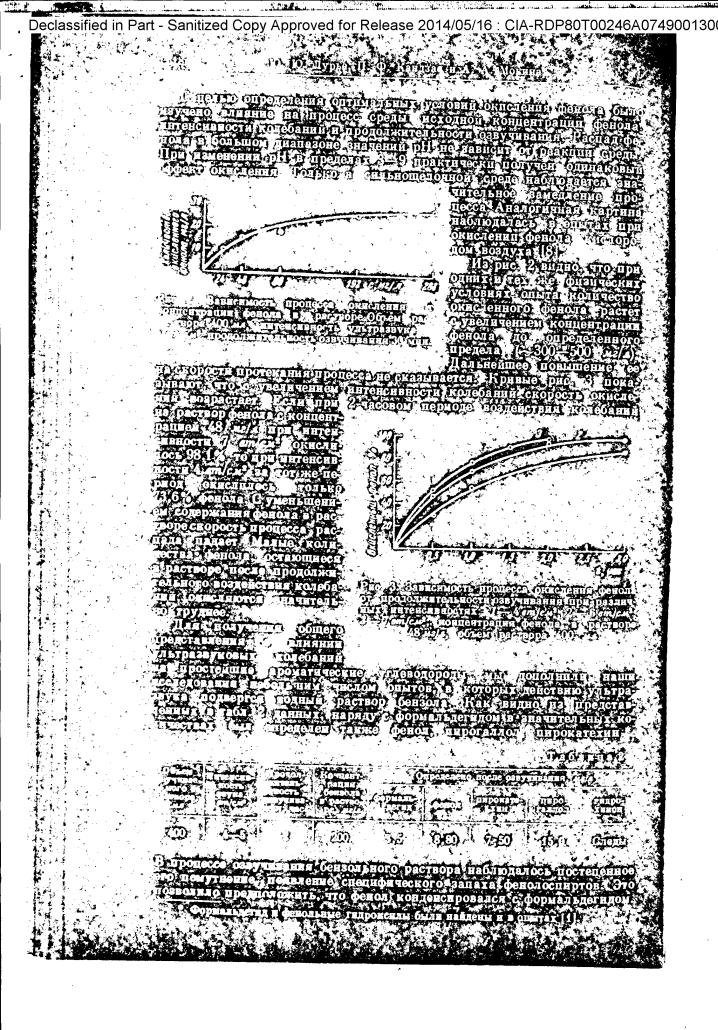
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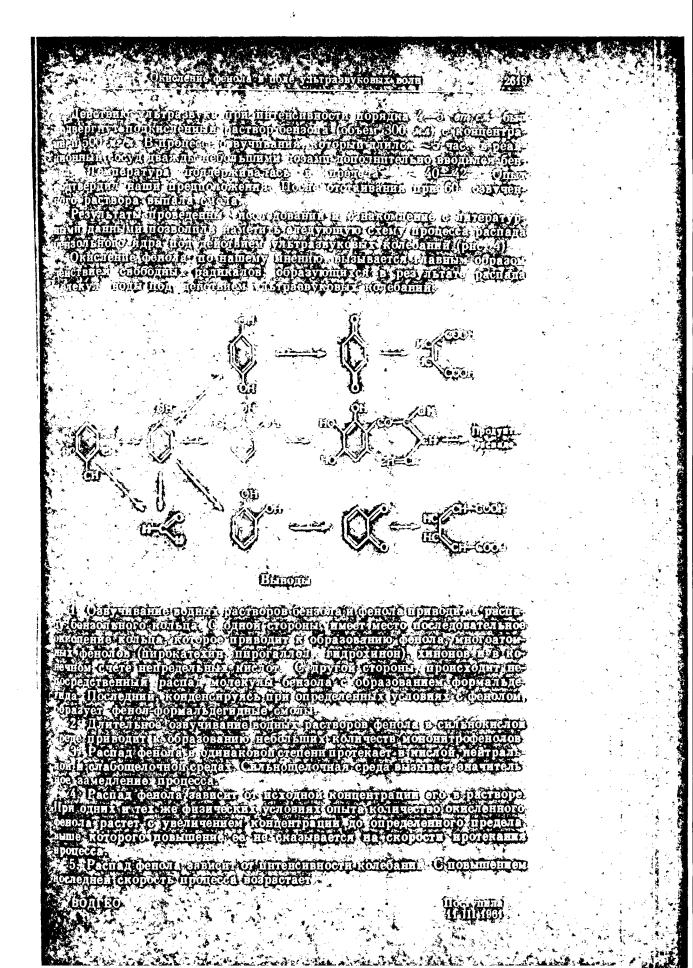
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